09/857382
JC18 Rec'd PCT/PTO 01 JUN 2001

Hydrophilic Member

BACKGROUND OF THE INVENTION

Technical Field of the Invention

This invention relates to a hydrophilic member and especially to a hydrophilic member having superior hydrophilic restoration properties.

Description of Relevant

Background Art

Japanese Unexamined Patent Publication Numbers Hei 9-278431, Hei 9-295363, Hei 10-36144, and Hei 10-231146 are known as background art having hydrophilic and anti-fogging properties on the substrate surfaces of glass and the like.

Japanese Unexamined Patent Publication Number Hei 9-278431 discloses the application, on a substrate surface, of a surface treatment agent including phosphoric acids or salts thereof, soluble aluminum compounds, water-soluble silicates, surface active agents, and solvents. The mean surface roughness of the hydrophilic film is 0.5 to 500 nm.

Japanese Unexamined Patent Publication Number Hei 9-295363 discloses a film of titanium oxide or tin oxide formed on a substrate surface, having a mean surface roughness of at least 1 μm.

Japanese Unexamined Patent Publication Number Hei 10-36144 discloses a photocatalyst film such as titanium oxide (TiO_2) formed on a glass substrate surface and a porous inorganic oxide film such as silicon oxide (SiO_2) formed on the surface of the photocatalyst film.

Japanese Unexamined Patent Publication Number Hei 10-231146 discloses an alkali barrier film and a photocatalyst film formed on the surface of a glass substrate. The mean surface roughness of the photocatalyst film is from1.5 to 80 nm.

The art disclosed in the above-mentioned Japanese Unexamined Patent Publication Number Hei 9-278431 is not practical since both the chemical durability and wear resistance of the hydrophilic film are low. The art disclosed in the above-mentioned Japanese Unexamined Patent Publication Number Hei 9-295363 is not applicable to the surface of a transparent substrate such as a glass plate because the mean surface roughness (Ra) of the hydrophilic film is greater than or equal to 1 μm, preferably greater than or equal to 4 μm, and the transparency thereof is low (high haze). With regards to the art disclosed in Japanese Unexamined Patent Publication Number Hei 10-36144, since wear resistance of the hydrophilic film is low because of the porosity thereof, hydrophilic function thereof is lost and is not easily recovered when contamination such as oil enters into the pores. With respect to the art disclosed in Japanese Unexamined Patent Publication Number Hei 10-231146, time is needed for production because the hydrophilic film is formed of a plurality of layers.

Moreover, with each of the above-disclosed background ~~prior~~ arts, a hydrophilic film is formed on the surface of a substrate and hydrophilic properties are further improved by making the surface have

Marked up copy

minute irregularities. However, in the case of a contaminated substrate, there is a drawback of slow restoration of the hydrophilic properties after washing of the substrate surface with a detergent.

For example, since a surface such as that of a windshield or a mirror provided with a lavatory is easily contaminated, it is frequently washed with a detergent. Unfortunately, restoration of hydrophilic properties after washing is slow, leading to minute water drops easily adhering to the surface and anti-fogging properties fade.

Summary

Disclosure of the Invention

In order to resolve the problems mentioned above, according to the present invention, there is provided a hydrophilic member, comprising a tin oxide layer formed on a surface of a substrate directly or through an undercoat film in between acting as a barrier against alkali, and an overcoat layer formed on the surface of the tin oxide layer, wherein the overcoat layer is selected from at least one of silicon oxide, aluminum oxide, zirconium oxide, ceric oxide, and titanium oxide. Furthermore, the mean surface roughness (Ra) of the top surface thereof is within a range of from 0.5 to 25 nm.

The mean surface roughness (Ra) is preferably within a range of from 0.5 to 25 nm, more preferably within a range of 5 to 15 nm. The long-term stability of the hydrophilic performance is further improved within this range.

If only a tin oxide (SnO_2) layer is formed on the surface of the substrate and the surface of this tin oxide (SnO_2) layer is rough, hydrophilic properties are displayed, as mentioned in the prior art (Unexamined Patent Publication Number Hei 9-295363). Unfortunately, upon washing the surface once with bath soap, the contact angle with water becomes 70° to 80°.

On the other hand, when a thin film such as a film of silicon oxide (SiO_2) is formed on the surface of the above-mentioned tin oxide (SnO_2) layer, the post-washing contact angle with water becomes less than 10°.

It is conceivable that the reason is because super-hydrophilic properties are present after washing since, from the aspect of surface polarity, tin oxide (SnO_2) and silicon oxide (SiO_2) have opposite polarities and bath soap is anionic.

It is preferable that the above-mentioned tin oxide (SnO_2) layer has a rutile structure. By making the tin oxide (SnO_2) to have a rutile structure, it is possible to form a polycrystalline thin film having a surface of preferable irregularities.

Moreover, by making the mean surface roughness (R_a) of the tin oxide (SnO_2) layer to be from 0.5 to 25 nm and transferring these irregularities to the top surface, it is possible to make the mean surface roughness (R_a) of the top surface to be from 0.5 to 25 nm.

It is not preferable that the mean surface roughness (R_a) be less than 0.5 nm, because effective

irregularities which improve long-term maintainability of hydrophilic properties and functions would not be formed. It is also not preferable for the mean surface roughness (R_a) to exceed 25 nm, in which case irregularities would be too great and transparency lost, or the long-term stability of the hydrophilic function would be lowered.

Additionally, it is preferable to make the mean spacing (S_m) of the irregularities to be from 4 to 300 nm. It is not preferable for the mean spacing (S_m) of the irregularities to be either less than 4 nm or greater than 300 nm, which would result in reduction of the long-term stability of hydrophilic performance and anti-fogging performance. The mean spacing (S_m) of the irregularities is more preferably from 5 to 150 nm. Within this range, the long-term stability of hydrophilic performance is further improved.

As a method of indicating the mean surface roughness (R_a), arithmetical mean surface roughness (R_a) as defined by JIS B0601 (1994) is used. The value (nm) of arithmetical mean surface roughness is expressed as "the absolute value of the deviation from the mean line", and is rendered by the following equation 1.

[equation 1] $$Ra = \frac{1}{L}\int_0^L |f(x)|dx$$

L : reference length

f(x) : roughness curve expression taking X-axis in the direction of mean line and Y-axis in the direction of longitudinal magnification of the sampled part

Moreover, the mean spacing of irregularities S_m, too, is defined by JIS B0601 (1994). The arithmetical mean value (nm) of irregularities is expressed as "the mean value of the spacing between cycles of peaks and valleys obtained from the point where the roughness curve and the mean line cross", and is rendered by the following equation 2.

[equation 2] $$Sm = \frac{1}{n}\sum_{i=1}^{n} Smi$$

S_{mi} : spacing of irregularities (nm)

n: number of spacings of irregularities within the reference length

It is preferable for the thickness of the tin oxide film or layer (SnO_2) to be from 10 to 800 nm, and for the thickness of the overcoat layer of silicon oxide film (SiO_2) or the like to be from 0.1 to 100 nm.

When the thickness of the tin oxide is less than or greater than this range, the desired irregularities cannot be obtained. That is, deviation outside of this range is not preferable because,

when the thickness of the tin oxide is smaller than this range, then a film of uniform thickness will not be realized; and when the thickness of the tin oxide is larger than this range, then the spacing of irregularities will become too large.

A film mainly comprised of common silicon oxide is preferable as the undercoat for the alkali barrier. Additives such as P (phosphorous) and B (boron) may be added, and oxide compounds of tin oxide may be used as needed.

The undercoat film for the alkali barrier may be formed using known processes. Examples include the sol-gel process, liquid phase deposition method, vacuum film forming method, baking method, spray coating method, and CVD (chemical vapor deposition) method.

It is preferable that the undercoat film for the alkali film barrier be at least 10 nm yet not greater than 300 nm. A thickness less than 10 nm is not preferable because it is insufficient for producing an effective alkali barrier. Additionally, a thickness greater than 300 nm is not preferable because interference colors frequently become noticeable and it becomes difficult to control the optical characteristics of a glass plate.

Glass mainly comprised of silicon oxide (SiO_2), tile, ceramics, or a metal plate is suitable for use as the substrate. Moreover, a hydrophilic member according to the present invention may be applied to mirrors, for example.

Brief Descriptions of the Drawings

Figures 1(a) and 1(b) are, respectively, enlarged cross-sectional views of a hydrophilic members according to the present invention, the member of Fig. 1(b) including an undercoat film not included in the member of Fig. 1(a).

Detailed Description of **Preferred Embodiment to Implement the Invention**

Hereinbelow, explanation will be made of the preferred embodiments of the present invention, based upon the attached drawings.

In the embodiment shown in Figure 1(a), the hydrophilic member comprises a film of tin oxide (SnO_2) 2 formed on the surface of a glass plate 1 as a substrate and a film of silicon oxide (SiO_2) 3 as an overcoat layer formed on the surface of this tin oxide (SnO_2) film 2.

In the embodiment shown in Figure 1(b), an undercoat film 4 stands between the glass plate1 and the tin oxide (SnO_2) film 2 to prevent alkalis such as Na from escaping out of the glass plate 1.

In Figure 1, R_a is the mean surface roughness and Sm indicates the mean spacing of the irregularities.

Soda glass, which has SiO_2 as its main component, is used as the glass plate 1. The tin oxide (SnO_2) film 2 is formed by a well-known process such as the sol-gel process, liquid phase deposition method, vacuum film forming method, baking method, spray coating method, CVD (chemical vapor deposition) method, or sputtering method. The thickness ranges from 10 to 800

nm and the mean surface roughness (R_a) ranges from 0.5 to 25 nm. The film of tin oxide (SnO_2) 2 has a rutile structure.

The film of silicon oxide (SiO_2) 3 has a thickness ranging from 0.1 through 100 nm and is formed by a well-known process such as the sol-gel process, liquid phase deposition method, vacuum film forming method, baking method, spray coating method, chemical vapor deposition method, or sputtering method. In addition, since the silicon oxide (SiO_2) film 3 is formed on the tin oxide (SnO_2) film 2, the irregularities of the tin oxide (SnO_2) film 2 are transferred just as they are, and the range of the mean surface roughness (R_a) of the surface of the silicon oxide (SiO_2) film 3 also becomes within the range of 0.5 to 25 nm.

The mean spacing (S_m) of irregularities preferably ranges from 4 to 300 nm. It is not desirable that the spacing deviate from this range because the long-term stability of the hydrophilic properties is low outside of the range.

By forming minute irregularities on the surface, the hydrophilic properties of the surface can be further improved.

That is, when the surface area becomes larger by r times due to formation of minute irregularities on the surface, $\cos\theta' = r \cos\theta$ ($90° > \theta > \theta'$) is established by Wenzel's formula, in which the contact angle of water at the time of the flat surface is θ and the contact angle of water at the time of forming irregularities is θ'. However, it is not the case when the contact angle θ deviates greatly from 90 degrees.

For example, forming irregularities on the surface of a member having a contact angle of 30° with respect to water when the surface is flat, and taking the surface area to be multiplied 1.1 times, then, from the above equation, $\cos\theta' = 1.1 \cos 30° = 0.935$, and from this it is determined that $\theta' = 17.7°$. Similarly, when the surface area is multiplied by 1.15, θ' becomes 5.2°. However, this equation is not necessarily established when θ is small, however, as a tendency, θ' becomes smaller by the provisions of irregularities.

That is, by the formation of minute irregularities on the surface, the hydrophilic surface becomes all-the-more hydrophilic.

On the other hand, as the undercoat film 4 for an alkali barrier, a thin film with silicon oxide as the main component or a compound oxide film comprised of silicon oxide and tin oxide, a film of silicon oxide which includes carbon, or layers of a film with tin oxide as the main components and a film with silicon oxide as the main component, or the like may be used.

For example, a compound oxide film comprised of silicon oxide and tin oxide or a film of silicon oxide which includes carbon has a refractive index which is between that of the glass plate 1 and the tin oxide film 2. Therefore, an even more preferable appearance can be obtained. That is, by having an undercoat film with an intermediate refractive index, it is possible to control interference color changes (color inconsistencies) arising from irregular thickness of the tin oxide

film, as well as neutralize reflection hues.

In the case where the undercoat film is a layered body of, for example, a film whose main component is tin oxide and a film whose main component is silicon oxide, because the apparent refractive index of the layered body is between the refractive index of the glass plate 1 and the refractive index of the tin oxide film 2 by adjusting the thickness of the respective films, the functions of the above-mentioned undercoat film with an intermediate refractive index can be obtained.

In the case where the hydrophilic member having the above-mentioned structure is applied to a mirror, a thin film of metal, for example, silver, is formed on the rear surface of the glass plate 1, between the glass plate 1 and the undercoat film 4; or, in the case of no undercoat, between the glass plate 1 and tin oxide (SnO_2) film 2.

Next, explanation will be made of processes for the formation of films occurring with the preferred embodiment s of the present invention and comparative examples. Specifically, using a film-forming apparatus (not shown), ~~the~~ a sample of embodiment 1 was made by forming, in order, a film of tin oxide and a film of silicon oxide on the surface of a glass plate. Using the same process as that of embodiment 1, the samples of embodiments 2, 3, 4, and 6 of embodiment 2 ~~were formed with~~, in order, a film of silicon oxide, a film of tin oxide and a film of silicon oxide on the surface of a glass plate. Using the same process as that of embodiment 1, the sample of embodiment sample ~~5 was~~ formed with, in order, a film of tin oxide, a film of silicon oxide, a film of tin oxide, and a film of silicon oxide on the surface of a glass plate.

Using the same process as that of embodiment 1, the sample of comparative example 1 was made with, in order, a film of tin oxide and a film of silicon oxide on the surface of a glass plate. The sample of comparative example 2 was made by conducting an etching process on the surface of an ordinary glass plate, in which the glass plate was immersed into an aqueous solution whose main component was hydrosilicofluoric acid, and on the surface of the glass plate were formed minute irregularities comprised of a porous film whose main component was silica. Using the same process as that of embodiment 1, the samples of comparative examples 4 and 5 were made by forming a tin oxide film on the surface of a glass plate. Comparative example 3 is an ordinary glass plate.

Next, the mean surface roughness (R_a) and the mean spacing (Sm) of the samples of the embodiments and the comparative examples were measured. These values were calculated from profile curves measured with an atomic force microscope (AFM) or an electron microscope.

Furthermore, the samples were washed with bath soap, and changes in the contact angles were measured so that wetting properties of the sample surface with respect to water could be confirmed. The angle of contact with water was measured immediately after washing, after the elapse of 2 hours, and after the elapse of 200 hours.

Tables 1 and 2, below, are, with regards to the hydrophilic member according to the present invention and the comparative examples, comparisons of changes of the contact angles with water

after washing with a detergent.

Table 1

		Embodiments Samples					
		1	2	3	4	5	6
mean surface roughness (nm)		10.0	3.0	7.0	13.0	25.0	8.5
mean spacing (nm)		40	30	65	110	150	70
change of contact angle (°)	immediately after washing	3.0	5.0	4.0	5.0	10.0	4.0
	2 hours after washing	4.0	10.0	6.0	6.0	12.0	6.0
	200 hours after washing	10.0	25.0	15.0	13.0	16.0	14.0
undercoat film composition		--	SiO_2	SiO_2	SiO_2	SnO_2/SiO_2	SiO_2
undercoat film thickness (nm)		--	20	20	20	25/25	20
SnO_2 film thickness (nm)		350	20	250	600	800	300
overcoat film thickness (nm)		20	20	50	20	50	50
remarks							

Table 2

		Comparative examples*				
		1	2	3	4	5
mean surface roughness (nm)		30.0	5.0	1.0	5.0	7.0
mean spacing (nm)		250	45	∞ (infinite)	50	70
change of contact angle (°)	immediately after washing	57.0	14.0	18.0	70.0	78.0
	2 hours after washing	65.0	18.0	20.0	70.0	79.0
	200 hours after washing	68.0	32.0	41.0	73.0	80.0
undercoat film composition		SnO_2/SiO_2	--	--	--	--
undercoat film thickness (nm)		25/25	--	--	--	--
SnO_2 film thickness (nm)		1000	--	--	60	150
overcoat film thickness (nm)		--	--	--	--	--
remarks		*Comparative example 2: glass plate on the surface of which are minute irregularities formed by etching Comparative example 3: ordinary glass plate Comparative example 4: glass plate with a film of tin oxide (SnO_2) provided on the surface Comparative example 5: glass plate with a film of tin oxide (SnO_2) provided on the surface				

Table 1 clearly shows that a hydrophilic member according to the present invention has an angle of contact with water of 10° or less just after washing, and the hydrophilic properties are durable over long periods of time.

On the other hand, Table 2 clearly shows that a common glass plates (comparative example 3) has an angle of contact with water of about 10° after washing, but the angle of contact gradually increases with time. This may be considered due to hydrophilic durability not being attained since the surface irregularities are small ($R_a \fallingdotseq 1nm$). A glass plate with fine irregularities formed on the surface by etching (comparative example 2) also has a contact angle with water of about 10°, but the angle of contact gradually increases with the elapse of time. This is presumably due to durability worsening because the spacing of irregularities is too small in relation to the surface irregularities, and the hydrophilic functions decreasing over time.

Moreover, in the case where the thickness of the tin oxide (SnO_2) film exceeds the range of the present invention (comparative example 1), since the spacing of irregularities on the surface becomes large ($S_m > 300$ nm), the spacing of irregularities on the surface of the silicon oxide film (SiO_2) becomes large, resulting in hydrophilic properties not able to be attained. Furthermore, when a film of tin oxide (SnO_2) only is formed on a glass plate (comparative examples 4 and 5), the angle of contact with water after washing is 70° or greater and hydrophilic properties are not manifested, regardless of the thickness of the tin oxide film (SnO_2). This is presumably due to the nature of the tin oxide (SnO_2) film itself, regardless of the surface shape.

Sample
Embodiment 6 is a mirror formed with a film of nearly ~~the same~~ composition as comparative example 3 on the surface of a glass plate having a silvered rear surface. This mirror surface does not fog at all, even when breath is exhaled thereupon, the angle of contact with water becomes 10° or less just after washing, and it maintains hydrophilic properties over long periods. Accordingly, the mirror of embodiment 6 has high hydrophilic properties, and exhibits desirable hydrophilic retention properties.

Embodiment sample

, i.e. the film characteristics are all the same, except that the SnO_2 film thickness is 300nm rather than 250nm.

Industrial applicability

As explained above, according to the first aspect of the above-mentioned hydrophilic member, the angle of contact with respect to water becomes small, allowing still greater long-term stability of hydrophilic properties to be obtained.

According to the second aspect of the above-mentioned hydrophilic member, it is possible to form a polycrystalline film having a desirably irregular surface, while attaining the effects of the above-mentioned first aspect.

According to the third aspect of the above-mentioned hydrophilic member, while attaining the effects of the above-mentioned first and second aspects, hydrophilic effects occurring on the top surface can be sufficiently attained, yet recovery of hydrophilic properties after washing will occur

within an extremely short period of time, and the retention of the hydrophilic properties is high.

According to the fourth aspect of the above hydrophilic members, it is possible to maintain hydrophilic properties over a long period of time, while attaining the respective effects of any one of the above-mentioned first, second, or third aspects.

According to the fifth aspect of the above-mentioned hydrophilic member, it is possible to form a desired hydrophilic film while attaining the respective effects of any one of the above-mentioned first through fourth aspects.

According to the sixth aspect of the above-mentioned hydrophilic member, it is possible to obtain desired irregularities while attaining the respective effects of any one of the above-mentioned first through fifth aspects.

According to the seventh aspect of the above-mentioned hydrophobic member, while attaining the respective effects of any one of the above-mentioned first through sixth aspects, it is possible to control interference color changes (color irregularities) as well as neutralize reflection hues, since the refractive index of the undercoat film is between the refractive index /indices of the glass plate and the tin oxide film.

According to the eighth aspect of the above-mentioned hydrophilic members, while attaining the respective effects of any one of the above-mentioned first through seventh aspects, it is possible to control interference color changes (color irregularities) as well as neutralize reflection hues, since the apparent refractive index of the layered film is between the refractive index /indices of the glass plate and the tin oxide film.

According to the ninth aspect of the above-mentioned hydrophilic member, while attaining the respective effects of any one of the above-mentioned first through eighth aspects, it is possible to make effective applications to mirrors, windshields, anti-fogging/anti-fouling glass for construction, spectacles, lenses, tile, metal plates, and the like.

According to the tenth aspect of the above-mentioned hydrophilic member, while attaining the respective effects of any one of the above-mentioned first through ninth aspects, it is possible to make effective applications to automobile door mirrors, bathroom mirrors, and the like.

Although there have been described what are the present embodiments of the invention, it will be understood by persons skilled in the art that variations and modifications may be made thereto without departing from the gist, spirit or essence of the invention. The scope of the invention is indicated by the appended claims.

What is claimed is:

1. A hydrophilic member comprising:

a tin oxide layer formed on a surface of a substrate directly or through an undercoat film acting as a barrier against alkali and; and

an overcoat layer formed on the surface of said tin oxide layer, wherein said overcoat layer is selected from at least one of silicon oxide, aluminum oxide, zirconium oxide, ceric oxide, and titanium oxide, and the mean surface roughness (R_a) of the top surface thereof is within a range of 0.5 to 25 nm.

layer

2. A hydrophilic member according to claim 1, wherein said tin oxide (SnO_2) has a rutile structure.

layer

3. A hydrophilic member according to either of claim 1 or claim 2, wherein the mean surface roughness (R_a) of said tin oxide (SnO_2) is also within a range of from 0.5 to 25 nm, and thereby the mean surface roughness (R_a) of the top surface is within a range of 0.5 to 25 nm.

claim 1

4. A hydrophilic member according to any one of claims 1 through 3, wherein the mean spacing (S_m) of the irregularities of the top surface is within a range of 4 nm to 300 nm.

of said overcoat layer

claim 1

5. A hydrophilic member according to any one of claims 1 through 4, wherein said tin oxide layer has a thickness of within a range of 10 to 800 nm.

claim 1

6. A hydrophilic member according to any one of claims 1 through 5, wherein said overcoat layer has a thickness of within a range of 0.1 to 100nm.

claim 12

7. A hydrophilic member according to any one of claims 1 through 6, wherein the refractive index of said undercoat film acting as a barrier against alkali is between the refractive index of the substrate and the refractive index of the tin oxide. layer

claim 12

8. A hydrophilic member according to any one of claims 1 through 7, wherein said undercoat film is a layered body of tin oxide and silicon oxide.

claim 1

9. A hydrophilic member according to one of claims 1 through 8, wherein said substrate is glass the main component of which is silicon oxide; tile; ceramic; or a metal plate.

and

selected from the group consisting of:

10. A hydrophilic member according to any one of claims 1 through 9 Claim 1, wherein said hydrophilic member is a mirror having a thin metal film formed on the rear surface thereof, between the substrate and the tin oxide layer, or between the undercoat film and the tin oxide layer.

11. A hydrophilic member according to Claim 1, wherein said overcoat layer is formed directly on the surface of the substrate.

12. A hydrophilic member according to claim 1, further including an undercoat film disposed between the surface of said substrate and said tin oxide layer, said undercoat film acting as a barrier against alkali.

13. A hydrophilic member according to Claim 12, wherein said hydrophilic member is a mirror having a thin metal film formed on the surface thereof, between the undercoat film and the tin oxide layer.

Abstract

A hydrophilic member is provided wherein the restoration of hydrophilic properties after washing occurs in an extremely short amount of time, yet the retention effect of the recovered hydrophilic properties is high. On the surface of glass plate 1, which is used as a substrate, is formed a tin oxide (SnO_2) film 2, and on the surface of this tin oxide (SnO_2) film 2 is formed, as an overcoat layer, a silicon oxide (SiO_2) film 3. Soda glass which has SiO_2 as its main component is used as the glass plate 1. The tin oxide (SnO_2) film 2 is formed, for example, by the chemical vapor deposition method, the thickness of the film being from 10 to 800 nm and the mean surface roughness (R_a) of the surface being from 0.5 through 25nm. Furthermore, the silicon oxide (SiO_2) film 3 is formed by the sputtering method, the thickness being from 0.1 to 100 nm. Moreover, since the silicon oxide (SiO_2) film 3 is formed on the tin oxide (SnO_2) film 2, the irregularities of the tin oxide film (SnO_2) 2 are transferred just as they are, which makes the silicon oxide (SiO_2) film have a mean surface roughness (R_a) of from 0.5 through 25 nm.

corresponding

PRTS

09/857382
Rec'd PCT/PTO 01 JUN 2001

Hydrophilic Member

Technical Field of the Invention

This invention relates to a hydrophilic member and especially to a hydrophilic member having superior hydrophilic restoration properties.

Background Art

Sub A3

Japanese Unexamined Patent Publication Numbers Hei 9-278431, Hei 9-295363, Hei 10-36144, and Hei 10-231146 are known as background art having hydrophilic and anti-fogging properties on the substrate surfaces of glass and the like.

Japanese Unexamined Patent Publication Number Hei 9-278431 discloses the application, on a substrate surface, of a surface treatment agent including phosphoric acids or salts thereof, soluble aluminum compounds, water-soluble silicates, surface active agents, and solvents. The mean surface roughness of the hydrophilic film is 0.5 to 500 nm.

Japanese Unexamined Patent Publication Number Hei 9-295363 discloses a film of titanium oxide or tin oxide formed on a substrate surface, having a mean surface roughness of at least 1 μm.

Japanese Unexamined Patent Publication Number Hei 10-36144 discloses a photocatalyst film such as titanium oxide (TiO_2) formed on a glass substrate surface and a porous inorganic oxide film such as silicon oxide (SiO_2) formed on the surface of the photocatalyst film.

Japanese Unexamined Patent Publication Number Hei 10-231146 discloses an alkali barrier film and a photocatalyst film formed on the surface of a glass substrate. The mean surface roughness of the photocatalyst film is from1.5 to 80 nm.

The art disclosed in the above-mentioned Japanese Unexamined Patent Publication Number Hei 9-278431 is not practical since both the chemical durability and wear resistance of the hydrophilic film are low. The art disclosed in the above-mentioned Japanese Unexamined Patent Publication Number Hei 9-295363 is not applicable to the surface of a transparent substrate such as a glass plate because the mean surface roughness (Ra) of the hydrophilic film is greater than or equal to 1 μm, preferably greater than or equal to 4 μm, and the transparency thereof is low (high haze). With regards to the art disclosed in Japanese Unexamined Patent Publication Number Hei 10-36144, since wear resistance of the hydrophilic film is low because of the porosity thereof, hydrophilic function thereof is lost and is not easily recovered when contamination such as oil enters into the pores. With respect to the art disclosed in Japanese Unexamined Patent Publication Number Hei 10-231146, time is needed for production because the hydrophilic film is formed of a plurality of layers.

Moreover, with each of the above-disclosed prior arts, a hydrophilic film is formed on the surface of a substrate and hydrophilic properties are further improved by making the surface have

minute irregularities. However, in the case of a contaminated substrate, there is a drawback of slow restoration of the hydrophilic properties after washing of the substrate surface with a detergent.

For example, since a surface such as that of a windshield or a mirror provided with a lavatory is easily contaminated, it is frequently washed with a detergent. Unfortunately, restoration of hydrophilic properties after washing is slow, leading to minute water drops easily adhering to the surface and anti-fogging properties fade.

Disclosure of the Invention

In order to resolve the problems mentioned above, according to the present invention, there is provided a hydrophilic member, comprising a tin oxide layer formed on a surface of a substrate directly or through an undercoat film in between acting as a barrier against alkali, and an overcoat layer formed on the surface of the tin oxide layer, wherein the overcoat layer is selected from at least one of silicon oxide, aluminum oxide, zirconium oxide, ceric oxide, and titanium oxide. Furthermore, the mean surface roughness (Ra) of the top surface thereof is within a range of from 0.5 to 25 nm.

The mean surface roughness (Ra) is preferably within a range of from 0.5 to 25 nm, more preferably within a range of 5 to 15 nm. The long-term stability of the hydrophilic performance is further improved within this range.

If only a tin oxide (SnO_2) layer is formed on the surface of the substrate and the surface of this tin oxide (SnO_2) layer is rough, hydrophilic properties are displayed, as mentioned in the prior art (Unexamined Patent Publication Number Hei 9-295363). Unfortunately, upon washing the surface once with bath soap, the contact angle with water becomes 70° to 80°.

On the other hand, when a thin film such as a film of silicon oxide (SiO_2) is formed on the surface of the above-mentioned tin oxide (SnO_2) layer, the post-washing contact angle with water becomes less than 10°.

It is conceivable that the reason is because super-hydrophilic properties are present after washing since, from the aspect of surface polarity, tin oxide (SnO_2) and silicon oxide (SiO_2) have opposite polarities and bath soap is anionic.

It is preferable that the above-mentioned tin oxide (SnO_2) has a rutile structure. By making the tin oxide (SnO_2) to have a rutile structure, it is possible to form a polycrystalline thin film having a surface of preferable irregularities.

Moreover, by making the mean surface roughness (R_a) of the tin oxide (SnO_2) to be from 0.5 to 25 nm and transferring these irregularities to the top surface, it is possible to make the mean surface roughness (R_a) of the top surface to be from 0.5 to 25 nm.

It is not preferable that the mean surface roughness (R_a) be less than 0.5 nm, because effective

irregularities which improve long-term maintainability of hydrophilic properties and functions would not be formed. It is also not preferable for the mean surface roughness (R_a) to exceed 25 nm, in which case irregularities would be too great and transparency lost, or the long-term stability of the hydrophilic function would be lowered.

Additionally, it is preferable to make the mean spacing (S_m) of the irregularities to be from 4 to 300 nm. It is not preferable for the mean spacing (S_m) of the irregularities to be either less than 4 nm or greater than 300 nm, which would result in reduction of the long-term stability of hydrophilic performance and anti-fogging performance. The mean spacing (S_m) of the irregularities is more preferably from 5 to 150 nm. Within this range, the long-term stability of hydrophilic performance is further improved.

As a method of indicating the mean surface roughness (R_a), arithmetical mean surface roughness (R_a) as defined by JIS B0601 (1994) is used. The value (nm) of arithmetical mean surface roughness is expressed as "the absolute value of the deviation from the mean line", and is rendered by the following equation 1.

[equation 1] $$Ra = \frac{1}{L}\int_0^L |f(x)|dx$$

L : reference length

f(x) : roughness curve expression taking X-axis in the direction of mean line and Y-axis in the direction of longitudinal magnification of the sampled part

Moreover, the mean spacing of irregularities S_m, too, is defined by JIS B0601 (1994). The arithmetical mean value (nm) of irregularities is expressed as "the mean value of the spacing between cycles of peaks and valleys obtained from the point where the roughness curve and the mean line cross", and is rendered by the following equation 2.

[equation 2] $$Sm = \frac{1}{n}\sum_{i=1}^{n} Smi$$

S_{mi} : spacing of irregularities (nm)

n: number of spacings of irregularities within the reference length

It is preferable for the thickness of the tin oxide film (SnO_2) to be from 10 to 800 nm, and for the thickness of the overcoat layer of silicon oxide film (SiO_2) or the like to be from 0.1 to 100 nm.

When the thickness of the tin oxide is less than or greater than this range, the desired irregularities cannot be obtained. That is, deviation outside of this range is not preferable because,

when the thickness of the tin oxide is smaller than this range, then a film of uniform thickness will not be realized; and when the thickness of the tin oxide is larger than this range, then the spacing of irregularities will become too large.

A film mainly comprised of common silicon oxide is preferable as the undercoat for the alkali barrier. Additives such as P (phosphorous) and B (boron) may be added, and oxide compounds of tin oxide may be used as needed.

The undercoat film for the alkali barrier may be formed using known processes. Examples include the sol-gel process, liquid phase deposition method, vacuum film forming method, baking method, spray coating method, and CVD (chemical vapor deposition) method.

It is preferable that the undercoat film for the alkali film be at least 10 nm yet not greater than 300 nm. A thickness less than 10 nm is not preferable because it is insufficient for producing an effective alkali barrier. Additionally, a thickness greater than 300 nm is not preferable because interference colors frequently become noticeable and it becomes difficult to control the optical characteristics of a glass plate.

Glass mainly comprised of silicon oxide (SiO_2), tile, ceramics, or a metal plate is suitable for use as the substrate. Moreover, a hydrophilic member according to the present invention may be applied to mirrors, for example.

Brief Descriptions of the Drawings

Figures 1(a) and 1(b) are, respectively, enlarged cross-sectional views of a hydrophilic member according to the present invention.

Preferred Embodiment to Implement the Invention

Hereinbelow, explanation will be made of the preferred embodiment of the present invention, based upon the attached drawings.

In the embodiment shown in Figure 1(a), the hydrophilic member comprises a film of tin oxide (SnO_2) 2 formed on the surface of a glass plate 1 as a substrate and a film of silicon oxide (SiO_2) 3 as an overcoat layer formed on the surface of this tin oxide (SnO_2) film 2.

In the embodiment shown in Figure 1(b), an undercoat film 4 stands between the glass plate1 and the tin oxide (SnO_2) film 2 to prevent alkalis such as Na from escaping out of the glass plate 1.

In Figure 1, R_a is the mean surface roughness and Sm indicates the mean spacing of the irregularities.

Soda glass, which has SiO_2 as its main component, is used as the glass plate 1. The tin oxide (SnO_2) film 2 is formed by a well-known process such as the sol-gel process, liquid phase deposition method, vacuum film forming method, baking method, spray coating method, CVD (chemical vapor deposition) method, or sputtering method. The thickness ranges from 10 to 800

nm and the mean surface roughness (R_a) ranges from 0.5 to 25 nm. The film of tin oxide (SnO_2) 2 has a rutile structure.

The film of silicon oxide (SiO_2) 3 has a thickness ranging from 0.1 through 100 nm and is formed by a well-known process such as the sol-gel process, liquid phase deposition method, vacuum film forming method, baking method, spray coating method, chemical vapor deposition method, or sputtering method. In addition, since the silicon oxide (SiO_2) film 3 is formed on the tin oxide (SnO_2) film 2, the irregularities of the tin oxide (SnO_2) film 2 are transferred just as they are, and the range of the mean surface roughness (R_a) of the surface of the silicon oxide (SiO_2) film 3 also becomes within the range of 0.5 to 25 nm.

The mean spacing (S_m) of irregularities preferably ranges from 4 to 300 nm. It is not desirable that the spacing deviate from this range because the long-term stability of the hydrophilic properties is low.

By forming minute irregularities on the surface, the hydrophilic properties of the surface can be further improved.

That is, when the surface area becomes larger by r times due to formation of minute irregularities on the surface, $\cos\theta' = r\cos\theta$ ($90° > \theta > \theta'$) is established by Wenzel's formula, in which the contact angle of water at the time of the flat surface is θ and the contact angle of water at the time of forming irregularities is θ'. However, it is not the case when the contact angle θ deviates greatly from 90 degrees.

For example, forming irregularities on the surface of a member having a contact angle of 30° with respect to water when the surface is flat, and taking the surface area to be multiplied 1.1 times, then, from the above equation, $\cos\theta' = 1.1\cos 30° = 0.935$, and from this it is determined that $\theta' = 17.7°$. Similarly, when the surface area is multiplied by 1.15, θ' becomes 5.2°.

However, this equation is not necessarily established when θ is small, however, as a tendency, θ' becomes smaller by the provisions of irregularities.

That is, by the formation of minute irregularities on the surface, the hydrophilic surface becomes all-the-more hydrophilic.

On the other hand, as the undercoat film 4 for an alkali barrier, a thin film with silicon oxide as the main component or a compound oxide film comprised of silicon oxide and tin oxide, a film of silicon oxide which includes carbon, or layers of a film with tin oxide as the main components and a film with silicon oxide as the main component, or the like may be used.

For example, a compound oxide film comprised of silicon oxide and tin oxide or a film of silicon oxide which includes carbon has a refractive index which is between that of the glass plate 1 and the tin oxide film 2. Therefore, an even more preferable appearance can be obtained. That is, by having an undercoat film with an intermediate refractive index, it is possible to control interference color changes (color inconsistencies) arising from irregular thickness of the tin oxide

film, as well as neutralize reflection hues.

In the case where the undercoat film is a layered body of, for example, a film whose main component is tin oxide and a film whose main component is silicon oxide, because the apparent refractive index of the layered body is between the refractive index of the glass plate 1 and the refractive index of the tin oxide film 2 by adjusting the thickness of the respective films, the functions of the above-mentioned undercoat film with an intermediate refractive index can be obtained.

In the case where the hydrophilic member having the above-mentioned structure is applied to a mirror, a thin film of metal, for example, silver, is formed on the rear surface of the glass plate 1, between the glass plate 1 and the undercoat film 4; or, in the case of no undercoat, between the glass plate 1 and tin oxide (SnO_2) film 2.

Next, explanation will be made of processes for the formation of films occurring with the preferred embodiment of the present invention and comparative examples. Specifically, using a film-forming apparatus (not shown), the sample of embodiment 1 was made by forming, in order, a film of tin oxide and a film of silicon oxide on the surface of a glass plate. Using the same process as that of embodiment 1, the samples of embodiments 2, 3, 4, and 6 were formed with, in order, a film of tin oxide and a film of silicon oxide on the surface of a glass plate. Using the same process as that of embodiment 1, the sample of embodiment 5 was formed with, in order, a film of tin oxide, a film of silicon oxide, a film of tin oxide, and a film of silicon oxide on the surface of a glass plate.

Using the same process as that of embodiment 1, the sample of comparative example 1 was made with, in order, a film of tin oxide and a film of silicon oxide on the surface of a glass plate. The sample of comparative example 2 was made by conducting an etching process on the surface of an ordinary glass plate, in which the glass plate was immersed into an aqueous solution whose main component was hydrosilicofluoric acid, and on the surface of the glass plate were formed minute irregularities comprised of a porous film whose main component was silica. Using the same process as that of embodiment 1, the samples of comparative examples 4 and 5 were made by forming a tin oxide film on the surface of a glass plate.

Next, the mean surface roughness (R_a) and the mean spacing (Sm) of the samples of the embodiments and the comparative examples were measured. These values were calculated from profile curves measured with an atomic force microscope (AFM) or an electron microscope.

Furthermore, the samples were washed with bath soap, and changes in the contact angles were measured so that wetting properties of the sample surface with respect to water could be confirmed. The angle of contact with water was measured immediately after washing, after the elapse of 2 hours, and after the elapse of 200 hours.

Tables 1 and 2, below, are, with regards to the hydrophilic member according to the present invention and the comparative examples, comparisons of changes of the contact angles with water

after washing with a detergent.

Table 1

		Embodiments					
		1	2	3	4	5	6
mean surface roughness (nm)		10.0	3.0	7.0	13.0	25.0	8.5
mean spacing (nm)		40	30	65	110	150	70
change of contact angle (°)	immediately after washing	3.0	5.0	4.0	5.0	10.0	4.0
	2 hours after washing	4.0	10.0	6.0	6.0	12.0	6.0
	200 hours after washing	10.0	25.0	15.0	13.0	16.0	14.0
undercoat film composition		--	SiO_2	SiO_2	SiO_2	SnO_2/SiO_2	SiO_2
undercoat film thickness (nm)		--	20	20	20	25/25	20
SnO_2 film thickness (nm)		350	20	250	600	800	300
overcoat film thickness (nm)		20	20	50	20	50	50
remarks							

Table 2

		Comparative examples*				
		1	2	3	4	5
mean surface roughness (nm)		30.0	5.0	1.0	5.0	7.0
mean spacing (nm)		250	45	∞ (infinite)	50	70
change of contact angle (°)	immediately after washing	57.0	14.0	18.0	70.0	78.0
	2 hours after washing	65.0	18.0	20.0	70.0	79.0
	200 hours after washing	68.0	32.0	41.0	73.0	80.0
undercoat film composition		SnO_2/SiO_2	--	--	--	--
undercoat film thickness (nm)		25/25	--	--	--	--
SnO_2 film thickness (nm)		1000	--	--	60	150
overcoat film thickness (nm)		--	--	--	--	--
remarks		*Comparative example 2: glass plate on the surface of which are minute irregularities formed by etching Comparative example 3: ordinary glass plate Comparative example 4: glass plate with a film of tin oxide (SnO_2) provided on the surface Comparative example 5: glass plate with a film of tin oxide (SnO_2) provided on the surface				

Table 1 clearly shows that a hydrophilic member according to the present invention has an angle of contact with water of 10° or less just after washing, and the hydrophilic properties are durable over long periods of time.

On the other hand, Table 2 clearly shows that a common glass plates (comparative example 3) has an angle of contact with water of about 10° after washing, but the angle of contact gradually increases with time. This may be considered due to hydrophilic durability not being attained since the surface irregularities are small ($R_a \fallingdotseq 1$nm). A glass plate with fine irregularities formed on the surface by etching (comparative example 2) also has a contact angle with water of about 10°, but the angle of contact gradually increases with the elapse of time. This is presumably due to durability worsening because the spacing of irregularities is too small in relation to the surface irregularities, and the hydrophilic functions decreasing over time.

Moreover, in the case where the thickness of the tin oxide (SnO_2) film exceeds the range of the present invention (comparative example 1), since the spacing of irregularities on the surface becomes large (S_m > 300 nm), the spacing of irregularities on the surface of the silicon oxide film (SiO_2) becomes large, resulting in hydrophilic properties not able to be attained. Furthermore, when a film of tin oxide (SnO_2) only is formed on a glass plate (comparative examples 4 and 5), the angle of contact with water after washing is 70° or greater and hydrophilic properties are not manifested, regardless of the thickness of the tin oxide film (SnO_2). This is presumably due to the nature of the tin oxide (SnO_2) film itself, regardless of the surface shape.

Embodiment 6 is a mirror formed with a film of the same composition as comparative example 3 on the surface of a glass plate having a silvered rear surface. This mirror surface does not fog at all, even when breath is exhaled thereupon, the angle of contact with water becomes 10° or less just after washing, and it maintains hydrophilic properties over long periods. Accordingly, the mirror of embodiment 6 has high hydrophilic properties, and exhibits desirable hydrophilic retention properties.

Industrial applicability

As explained above, according to the first aspect of the above-mentioned hydrophilic member, the angle of contact with respect to water becomes small, allowing still greater long-term stability of hydrophilic properties to be obtained.

According to the second aspect of the above-mentioned hydrophilic member, it is possible to form a polycrystalline film having a desirably irregular surface, while attaining the effects of the above-mentioned first aspect.

According to the third aspect of the above-mentioned hydrophilic member, while attaining the effects of the above-mentioned first and second aspects, hydrophilic effects occurring on the top surface can be sufficiently attained, yet recovery of hydrophilic properties after washing will occur

within an extremely short period of time, and the retention of the hydrophilic properties is high.

According to the fourth aspect of the above hydrophilic members, it is possible to maintain hydrophilic properties over a long period of time, while attaining the respective effects of any one of the above-mentioned first, second, or third aspects.

According to the fifth aspect of the above-mentioned hydrophilic member, it is possible to form a desired hydrophilic film while attaining the respective effects of any one of the above-mentioned first through fourth aspects.

According to the sixth aspect of the above-mentioned hydrophilic member, it is possible to obtain desired irregularities while attaining the respective effects of any one of the above-mentioned first through fifth aspects.

According to the seventh aspect of the above-mentioned hydrophobic member, while attaining the respective effects of any one of the above-mentioned first through sixth aspects, it is possible to control interference color changes (color irregularities) as well as neutralize reflection hues, since the refractive index of the undercoat film is between the refractive index of the glass plate and the tin oxide film.

According to the eighth aspect of the above-mentioned hydrophilic members, while attaining the respective effects of any one of the above-mentioned first through seventh aspects, it is possible to control interference color changes (color irregularities) as well as neutralize reflection hues, since the apparent refractive index of the layered film is between the refractive index of the glass plate and the tin oxide film.

According to the ninth aspect of the above-mentioned hydrophilic member, while attaining the respective effects of any one of the above-mentioned first through eighth aspects, it is possible to make effective applications to mirrors, windshields, anti-fogging/anti-fouling glass for construction, spectacles, lenses, tile, metal plates, and the like.

According to the tenth aspect of the above-mentioned hydrophilic member, while attaining the respective effects of any one of the above-mentioned first through ninth aspects, it is possible to make effective applications to automobile door mirrors, bathroom mirrors, and the like.

What is claimed is:

1. A hydrophilic member comprising:

a tin oxide layer formed on a surface of a substrate directly or through an undercoat film acting as a barrier against alkali and;

an overcoat layer formed on the surface of said tin oxide layer, wherein said overcoat layer is selected from at least one of silicon oxide, aluminum oxide, zirconium oxide, ceric oxide, and titanium oxide, and the mean surface roughness (R_a) of the top surface thereof is within a range of 0.5 to 25 nm.

Sub A1

2. A hydrophilic member according to claim 1, wherein said tin oxide (SnO_2) has a rutile structure.

3. A hydrophilic member according to either of claim 1 or claim 2, wherein the mean surface roughness (R_a) of said tin oxide (SnO_2) is within a range of from 0.5 to 25 nm, and thereby the mean surface roughness (R_a) of the top surface is within a range of 0.5 to 25 nm.

4. A hydrophilic member according to any one of claims 1 through 3, wherein the mean spacing (S_m) of the irregularities of the top surface is within a range of 4 nm to 300 nm.

5. A hydrophilic member according to any one of claims 1 through 4, wherein said tin oxide layer has a thickness of within a range of 10 to 800 nm.

6. A hydrophilic member according to any one of claims 1 through 5, wherein said overcoat layer has a thickness of within a range of 0.1 to 100nm.

7. A hydrophilic member according to any one of claims 1 through 6, wherein the refractive index of said undercoat film acting as a barrier against alkali is between the refractive index of the substrate and the refractive index of the tin oxide.

8. A hydrophilic member according to any one of claims 1 through 7, wherein said undercoat film is a layered body of tin oxide and silicon oxide.

9. A hydrophilic member according to one of claims 1 through 8, wherein said substrate is glass the main component of which is silicon oxide; tile; ceramic; or a metal plate.

Cont

Sub

A1

10. A hydrophilic member according to any one of claims 1 through 9, wherein said hydrophilic member is a mirror having a thin metal film formed on the rear surface thereof, between the substrate and the tin oxide layer, or between the undercoat film and the tin oxide layer.

Abstract

A hydrophilic member is provided wherein the restoration of hydrophilic properties after washing occurs in an extremely short amount of time, yet the retention effect of the recovered hydrophilic properties is high. On the surface of glass plate 1, which is used as a substrate, is formed a tin oxide (SnO_2) film 2, and on the surface of this tin oxide (SnO_2) film 2 is formed, as an overcoat layer, a silicon oxide (SiO_2) film 3. Soda glass which has SiO_2 as its main component is used as the glass plate 1. The tin oxide (SnO_2) film 2 is formed, for example, by the chemical vapor deposition method, the thickness of the film being from 10 to 800 nm and the mean surface roughness (R_a) of the surface being from 0.5 through 25nm. Furthermore, the silicon oxide (SiO_2) film 3 is formed by the sputtering method, the thickness being from 0.1 to 100 nm. Moreover, since the silicon oxide (SiO_2) film 3 is formed on the tin oxide (SnO_2) film 2, the irregularities of the tin oxide film (SnO_2) 2 are transferred just as they are, which makes the silicon oxide (SiO_2) film have a mean surface roughness (R_a) of from 0.5 through 25 nm.

Sub A2